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UF_5, A NEW FLUORIDE OF URANIUM

By Aristid V. Grosse

There are two known fluorides of uranium, with widely different physical and chemical properties. Uranium tetrafluoride, UF_4, has been known for a long time. It is a green solid, melts at about 1,000°C, is insoluble in water, and chemically is rather inert. Uranium hexafluoride, UF_6, discovered by O. Ruff* in 1909, is a very reactive colorless gas or very volatile crystalline solid. It melts at 69°, has a vapor pressure of 1 atmosphere at 56°and is thermally stable up to at least 400°C. It is the most volatile compound of uranium and is the only uranium compound available for methods of isotope separation where a gas vapor is required.

Uranium pentafluoride, of the empirical composition UF_5, was discovered in the course of an investigation which had as its object to effect an exchange of uranium between uranium hexa- and tetrafluoride. †This was of interest in connection with enriching UF_6 depleted in U 235 in the course of isotope separation, by means of UF_4 of natural isotope composition.

It was first observed that when powdered anhydrous UF_4 (obtained by dehydrating the crystalline $2UF_4 \cdot 5H_2O$) is heated to 80° with liquid colorless UF_6, in a glass tube, it remains apparently insoluble, but gradually loses its original bright green color and assumes a greyish tinge. At the same time the UF_6 remains perfectly colorless and clear. On distilling off all the UF_6, a spongy-looking, dirty grey-green solid remains. On adding a few drops of water to this powder the original green color is restored, and simultaneously a clear yellow solution of hexavalent uranium is formed.

These facts indicated the possibility of compound formation between the two fluorides.

This possibility became a certainty when UF_4 was heated with excess liquid UF_6 to 95 to 100°C for periods of 20 to 100 hours. It was found that UF_6 reacts with UF_4 according to the equation

$$UF_6 + UF_4 \rightarrow 2\ UF_5,$$

forming a new fluoride of uranium. This compound is a greyish to white solid; some preparations appear to be crystalline. The pentafluoride readily disproportionates into UF_6 and UF_4 on heating, particularly under reduced pressure, and may be better formulated as a complex:

$$(UF_4 \cdot UF_6).$$

This complex does not noticeably disproportionate at 70° and 2 to 5 mm Hg pressure. Since this temperature is above the sublimation and melting point of UF_6, any excess of the latter may be readily separated from the complex by heating in a vacuum. However, the complex readily dissociates into its constituents on heating for periods of 1 to 2 hours at a temperature range of 175 to 300 at 2-mm pressure; the UF_6 elimination from the complex is complete at 300 to 400°C.

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*O. Ruff and A. Heinzelmann, Berichte 42: 495 (1909): Zeit. Anorg. Chem. 72, 63, (1911).

†See A. V. Grosse's paper on "Exchange of Uranium between UF_4 and UF_6."

The pentafluoride is violently decomposed by water in accordance with the equation

$$2UF_5 + 2\,H_2O \rightarrow UF_4 + UO_2F_2 + 4\,HF.$$

The green insoluble UF_4 can be easily separated from the yellow solution of uranyl fluoride. This affords a simple analytical method for determining the tetra- and hexavalent uranium content of the complex. However, the pentafluoride is not as sensitive to moisture in air as the hexafluoride is.

Preparation by Direct Addition

A typical experiment in the preparation of UF_5 by direct addition of UF_4 was made as follows: 2.0 millimoles, or 0.628 g, of anhydrous UF_4, e.g. $2UF_4 \cdot 5H_2O$, were heated with 15.0 millimoles, or 5.280 g, of UF_6 (resublimed over KF[‡]) for 100 hours to 100°C in a copper reaction vessel of about 25-cc capacity. (The vessel was made of copper tubing with silver-soldered copper ends. A brass valve, of the type used in refrigerators, was silver-soldered on at the top. The whole apparatus weighed about 30 g and had a free volume of about 25 cc. It readily withstood the few atmospheres pressure generated by excess UF_6 and could be easily weighed on an analytical balance. For drying, filling, and emptying the UF_6, it was attached to the usual type of vacuum line.)

After heating, the excess of UF_6 was pumped off at 100°C and 2-mm pressure: 12.9 millimoles, or 4.53 g, of unreacted UF_6 were recovered. The UF_4 retained 2.1 moles, or 0.738 g, of UF_6, so that the composition of the pentafluoride was

$$(UF_4)_{1.00} \cdot (UF_6)_{1.05}.$$

The slight excess of UF_6 may be due to either insufficient pumping, or to stronger adsorption of the last amounts, or to both.

On heating the pentafluoride for 2 hours to 300°C at 2-mm Hg, 0.67 g UF_6, or 90 per cent, of the complex's UF_6 content was recovered. To eliminate the residual UF_6, higher temperatures and/or longer heating periods were necessary.

It is possible that the pentafluoride may also be prepared by dehydro fluorinating the little-defined complex between UF_5 and hydrogen fluoride of the composition

$$UF_5, x\,HF.$$

This unanalyzed complex was obtained by O. Ruff, as an intermediate in his unsuccessful attempts to prepare UF_6 from the reaction of UCl_5 with hydrogen fluoride.

Acknowledgments

The pentafluoride was discovered in the course of studying the exchange of uranium between UF_4 and UF_6 during the period from November 1940 to February 1941, at the Department of Physics of Columbia University.

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[‡]The purification of UF_6 by means of alkali fluorides, which permits its easy handling in glass vessels will be described in a separate paper.

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